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**(TITLE UNCLASSIFIED)
EVALUATION OF
HIGH-ENERGY BINDER**

**P. L. ALLEN
E. K. IVES
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UNITED TECHNOLOGY CENTER**

**TECHNICAL REPORT AFRPL-TR-66-354
DECEMBER 1966**

Group 4
DOWNGRADED AT 3 YEAR INTERVALS
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P. L. Allen
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L. K. Asaoka

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FOREWORD

(U) This report is the third of three quarterly reports on Contract No. AF 04(611)-11404 under which United Technology Center (UTC) is conducting a program to evaluate the high-energy NF_2 binder, PBEP, in prototype propellant formulations. This report covers the experimental work conducted at UTC's Sunnyvale, California, research laboratories during the period 1 September 1966 through 30 November 1966. The work performed under this project is in response to requirements of AFFTC Project 3148, Program Element No. 62405184, BPSN 623148. Approving authority is Mr. Robert C. Corley, RPCS, AFFTC, Edwards Air Force Base, California.

(U) Publication of this report does not constitute Air Force approval of the findings or conclusions presented herein. It is published only for the exchange and stimulation of ideas.

Approving authority is
Mr. Corley

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CONFIDENTIAL ABSTRACT

(C) Work was continued on studying the cure problem of PBEP propellants. It now appears that a rapid reaction between the isocyanate curative and triol crosslinkers is the source of difficulty. It appears possible that this problem became enhanced by a change in PBEP during synthesis scaleup that resulted in a lower reactivity of the hydroxyl groups. Further investigations of the impact sensitivity of PBEP and PBEP propellants were made. No change in previously reported data was found, and it was concluded that neither PBEP nor propellant was unduly impact sensitive. Good cures were obtained on AlH_3 /PBEP propellant. Stress of 121 psi and strain of 52% were obtained on an ambient cured system. Preparation of HAP-containing propellant requires a dry atmosphere throughout the complete operation. The cured propellant also must be protected from moisture. Surveillance studies of 2-in. cubes have indicated that DBTDA cure catalyst has better aging characteristics.

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ABBREVIATIONS AND SYMBOLS

1, 2, 6-HT	1, 2, 6-hexanetriol
AlH ₃	aluminum hydride (C)
AP	ammonium perchlorate
BeH ₂	beryllium hydride (C)
DBTDA	dibutyltin diacetate
DBTDL	dibutyltin dilaurate
DTA	differential thermal analysis
DMM	3, 3'-dimethyl diphenyl methane 4, 4'-diisocyanate
FeAA	ferric acetylacetonate
HAP	hydroxylamine perchlorate
H ₁₂ MDI	4, 4'-methylene bis (cyclohexyl isocyanate)
N ₂ F ₄	tetrafluorohydrazine
NFPA	2, 3-bis (difluoramino) propyl acrylate (C)
NF ₂	nitrogen difluoride
PBEP	poly 1, 2-bis (difluoramino) 2, 3-epoxy propane (C)
TiCAA	titanium acetylacetonate
TDI	tolylene diisocyanate
TGA	thermal gravimetric analysis
TVOPA	1, 2, 3-tris [1, 2, -bis (difluoramino) vinoxyl] propane (C)
VaOAA	vanadium acetylacetonate

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SECTION I

INTRODUCTION

1. PROGRAM SCOPE

(C) Under Contract No. AF 04(611)-11404, UTC is conducting a research program to evaluate a high-energy NF_2 binder in both metallized and non-metallized propellants oxidized by conventional and high-energy oxidizers. The purpose of the program is the extension of the utility of the PBEP binder with state of the art fuels and advanced fuels to yield advanced propellants of high performance, high density, and high-performance efficiency. In addition to these objectives, the program also is designed to develop a high burning rate NF_2 propellant and to provide test data on the stability of NF_2 propellants. Work under this contract began on 1 March 1966.

(C) The program is divided into three phases. Phase I is concerned with the development of propellants with aluminum and boron as fuels Phase II is devoted to the exploitation of the PBEP binder as a high-energy replacement for existing high-performance systems. Aluminum hydride (AlH_3), beryllium, and beryllium hydride (BeH_2) fuels are to be formulated with a variety of oxidizers and plasticizers. Phase III is devoted to the development of techniques for measuring the stability of NF_2 propellants and for the characterization of these propellants using manometric and physical deterioration measurements.

(C) The primary goals of this work are:

- A. Development of a boron and aluminum propellant with a theoretical impulse of 300 sec.
- B. Development of a propellant with an impulse greater than current state of the art (265 sec) and a density greater than 0.065 lb/in.³
- C. Development of a propellant with a burning rate range of from 1.0 to 10.0 in./sec at 1,000 psi.
- D. Obtain data on the long-term aging stability of Domino propellants based on the PBEP binder.

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2. REPORT STATUS

(U) The present report covers the experimental work performed during the third quarter, 1 September 1966 to 30 November 1966. The reporting status for the program is presented graphically in figure 1.

	1966											1967
	M	A	M	J	J	A	S	O	N	D	J	F
Monthly Letter Report										10	11	12
Monthly Government-Furnished Propellant Report												
Quarterly Technical Report												
Final Technical Summary Report												

R-61228

Figure 1. Program Status Report

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SECTION II

TECHNICAL DISCUSSION

(C) PBEP is prepared by Shell Development Company by the direct addition of N_2F_4 to the unsaturated carbon-to-carbon double bonds in dehydrochlorinated polyepichlorohydrin which has been glycerol initiated. PBEP is currently synthesized in 1-liter reaction vessels by Shell Development and the Material which is then sent to UTC is a blend of a number of these batches. A normal shipment of PBEP contains 5 to 8 lb of PBEP from these various batch syntheses. Shell analysis of the PBEP received on this contract are shown in table I. PBEP lot No. 9557-99A with a molecular weight of 3,320 had the lowest molecular weight of any sample received during the program. The effect of this low molecular weight on the overall propellant properties at this time is unknown.

TABLE I
(U) PBEP LOT ANALYSIS*

	<u>9557-84</u>	<u>9357-998</u>
Total weight, g	2,948.4	3,628
Carbon, wt-%	26.5	26.6
Hydrogen, wt-%	3.3	3.2
Nitrogen, wt-%	15.8	15.4
Fluoride, wt-%	40.4	38.8
Elemental ratio, F/N	---	---
Molecular weight [†]	3,790	3,320
NCO equivalent, [‡] eq/100 g	0.075	0.108
Thermal Stability	~5.5	6.6
at 80° C, cc/g/100 hr	(200 hr)	(216 hr)

* Data supplied by Shell Development Company

† Mechrolab osmometer in ethylene chloride

‡ Determined by amount of TDI necessary to give maximum viscosity.

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1. PBEP STABILITY AND AGING STUDIES

(C) The JANAF vacuum stability apparatus was evaluated as a tool for measuring the thermal stability of PBEP samples during this report period. However, because of the difficulty of removing all the residual solvent from PBEP, the results of the test conducted with this equipment were inconclusive. The reproducibility was found to be very poor because of the lack of ability to compensate for the rapid evolution of solvent during the testing. However, further evaluation of the thermal gravimetric analysis (TGA) method for measuring thermal stability was conducted. The results of these tests are shown in figure 2. Duplicate runs on PBEP lot No. 9557-99A gave excellent reproducibility. The results of the TGA analysis on lot No. 9557-84A are also shown. Utilizing the slope of the percent of sample remaining per hr as a criteria for stability, it is apparent that the 99A lot is less stable than lot No. 9557-84A. Because of the reproducibility of the results of this study, TGA will be used in the future as the primary tool for measuring thermal stability of the neat PBEP samples.

(U) The JANAF vacuum stability apparatus is, however, being tested further as a tool for measuring the stability of PBEP propellant samples. A PBEP propellant, currently under test in this apparatus, indicate that this is a potentially useful tool for measuring the thermal stability of propellant where the residual solvent has been removed to a level that will not interfere with the final results of the test. However, no data on a complete run are available at this time.

(C) Data are now available on the results of the storage of the two 2-in. cubes that have been held for approximately 3 months at 35° C. Storage of these cubes was followed by X-ray analysis on a semimonthly basis. The zero time X-ray analysis for the cubes showed that formulation UTX-8422-5 which utilized FeAA as a cure catalyst had internal voids in the cube of approximately 0.05 to 0.01 in. in size. The other cube, UTX 8416-2, utilizing dibutyltin diacetate as a cure catalyst had some voids in it of approximately 0.05 to 0.025 in. in size. However, the surface area of the internal voids in UTX 8416 was equal to only 0.0235 in. as compared to the FeAA-containing cube where the surface area of the internal voids was equal to 0.112 in. During the first 2 months of storage, neither cube revealed any change from the baseline X-ray. However, at the end of 2-1/2 months the FeAA-containing cube, UTX 8422-5, showed a considerable increase in internal gas porosity. UTX 8416 still shows no change from the original porosity in the cube plus an increase in the number of voids present. Storage on both cubes is continuing until such time as it is felt that it would be hazardous to maintain the decomposing material in storage. There are at present three additional cubes ready to be placed in

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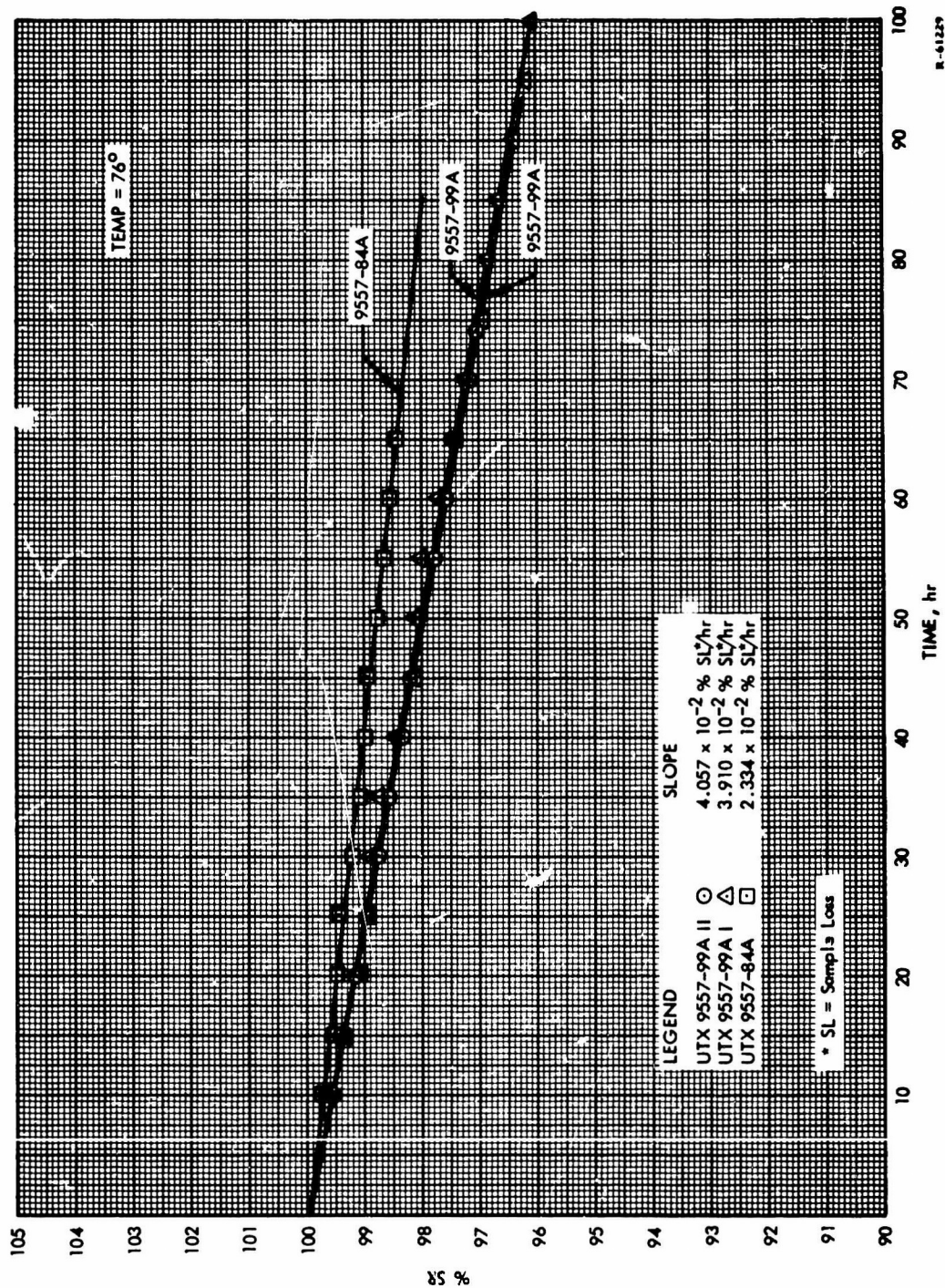


Figure 2. (U) Vacuum TGA Results of Neat PBEP

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storage, one of which contains tricresyl phosphate as stabilizer. Storage history of these cubes will be followed in the same manner as the previous two cubes.

2. IMPACT SENSITIVITY OF PBEP PROPELLANT

(U) The impact sensitivities of PBEP that have been reported by UTC have been obtained on an Olin Mathieson Impact Tester using an open cup method. It was felt that the properties of PBEP, such as its extremely high viscosity, placed this material more in the category of an uncured propellant rather than that of a liquid sample. However, as several companies have reported closed cup impact values for PBEP much lower than those reported by UTC's open cup data or by Shell Development's closed cup data, several lots of PBEP were reevaluated using open and closed cup methods. These data are listed in table II for the neat PBEP. Data on PBEP/TVOPA blends and on PBEP propellant are listed in table III.

(C) In table II both open cup and closed cup data are given. These tests were run on freshly stripped material by the same operator in the same time period. Where there is no closed cup data reported, it was because

TABLE II

(U) IMPACT SENSITIVITIES OF PBEP SAMPLES

PBEP Lot	Open Cup	Closed Cup	PBEP Lot	Open Cup	Closed Cup
	E ₅₀ kg-cm	E ₅₀ kg-cm		E ₅₀ kg-cm	E ₅₀ kg-cm
8976-110	6.0	---	9237-163A	11.6	35.2
8976-112	6.0	---	9165-107	14.3	---
8976-126	28.9	---	9088-180	17.0*	20.2†
8976-130	23.8	---	9088-180	60 - 90‡	---
8976-182	---	22.2	9088-180	18.4§	15.4
9305-8	55.4	27.6	9557-84	28.0	42.0
9305-9	20.2	---	9456-16	21.2	17.8
9305-14	16.0	---	9537-14	---	25.8
9237-68D	17.8	41.4	9557-84	40.0	42.0
9237-86B	17.3	21.8			

* Shell stripped material

† An impact of 5.8 obtained after one month ambient aging

‡ Original values

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TABLE III
(U) IMPACT SENSITIVITIES OF GUMSTOCK AND PROPELLANT

<u>PBEP</u>	<u>E₅₀[*]</u> <u>kg-cm</u>	<u>PBEP/TVOPA</u>	<u>E₅₀[*]</u> <u>kg-cm</u>	<u>Propellant</u>	<u>E₅₀[*]</u> <u>kg-cm</u>
8976-126	28.9	1/1 (U) [†]	10.2	(U)	15.8
8976-126	---	1/1 (C) [‡]	17.2	(C)	27.6
8976-130	23.8	1/1 (U)	15.8	(U)	15.8
9165-107	14.3	---	---	UTX 8407 (U)	15.1
				UTX 8407 (C)	8.3/ 11.6/ 11.4/ 14.2/ 11.8
---	---	---	---	UTP 3001	24.4
9237-68D	17.8	1/1 (C)	10.2	(C)	15.0
9557-84	28.0	---	---	---	---
9456-16	17.8	---	---	UTX 8419-2	7.5
9088-180	90.0	1/1 (C)	120	(C)	31
9088-180	---	1/1 (C)	51	---	---
9088-180	---	1/1 (U)	51.0	---	---
		PBEP/OPE			
9165-107	14.3	1/1 (U)	3.0	---	---
		PBEP/OPE			
9088-180	---	1/1 (U)	12.0	---	---
9088-180	---	1/1 (C)	70	---	---
9088-180	18.4	1/1 (U)	40**	---	---
9088-180	---	1/1 (U) ^{††}	19.2	---	---
9557-84	40	---	---	UTX 8422 (C)	13.6/ 13.3/ 13.4

- * Open cup
- † Uncured
- ‡ Cured
- § Results of five batches
- ** Smoke at 8 kg-cm
- †† Closed cup
- ‡‡ Results of three batches

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of the lack of material to rerun the test, and these data are reported from the original work on PBEP. Of the numerous lots of PBEP retested, only three lots gave an impact value of less than 11.6 kg-cm by either open or closed cup methods. These lots were 8976-110, 8976-112, and 9088-180. Lot Nos. 8976-110 and 8976-112 were the first two samples of PBEP received. Lot No. 9088-180 gave a value of 5.8 kg-cm in a closed cup test once after the material had been aged for approximately 1 month at room temperature, in the neat stage. This value is therefore considered somewhat questionable as being representative of that of normal PBEP. Considerable variation was observed in lot No. 9088-180 over its test history. Impacts as high as 90 kg-cm and as low as 17 kg-cm were observed for this material. It is believed that the variation in these values is a result of the difficulty in obtaining reproducible samples of extremely viscous PBEP. However, from the testing at UTC, no samples of PBEP appear to be unduly sensitive to impact.

(U) A closed cup impact value for TVOPA of 2.66 kg-cm was obtained on a sample of Aerojet-synthesized material as compared with a previous value on Rohm and Haas-synthesized TVOPA of 1.5 kg-cm. These values are comparable and appear to be representative of the sensitivity of neat TVOPA.

(C) No explanation could be given for the low values for the impact sensitivity of PBEP reported by Rohm and Haas. However, because there is no need at UTC for manual handling of either PBEP or TVOPA, or the binder materials without being diluted by solvent, the impact sensitivity of the propellant appears to be more important than the sensitivity of the binder. Impact values for propellant such as those listed in table III usually fall between 8 to 16 kg-cm depending upon the lot of PBEP and the state of cure. Reproducibility of the impact values obtained from numerous batches of the PBEP propellant is indicative of the impact sensitivity that can be expected of PBEP-TVOPA propellant. The impact sensitivity range of the cured propellant permits manual handling such as for transportation purposes but does, however, preclude any manual trimming or sawing type of operations. It should be noted, however, that FBEP propellant has been successfully sawed and milled in the UTC remote milling facility without incident.

(U) It appears that the value of the sensitivity of PBEP will remain unresolved until different test techniques are devised for evaluation of the sensitivity of this type of material.

3. HAP/LMH-1 STUDIES

(C) Studies were continued during this quarter on the evaluation of AlH_3 and HAP in PBEP propellants. The AlH_3 /AP and the AlH_3 /HAP systems were both scaled up to the 50-g batch size in a micromixer.

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a. Curative and Catalyst Study

(C) HAP has been demonstrated to be incompatible with both TDI curative and FeAA as a cure catalyst. In the last report, the use of a difunctional isocyanate DMM and DBTDA as a catalyst was demonstrated. During this quarter, further studies were conducted to evaluate other curatives and cure catalysts. A series of mixes were formulated with H₁₂MDI, the diisocyanate produced by National Aniline Division of Allied Chemical Co. The cure catalysts which were tested were VaOAA, T₁₂ and DETDL. A complete list of ingredients and formulations (series 1 to 8) is given in table IV. As the HAP was added to the vanadium and titanium catalyzed mixes, immediate color change was observed which was ascribed tentatively to the reduction of the catalyst. All six hand mixes, however, cured firmly.

(U) The six mixes in series 132 were prepared to evaluate the aliphatic diisocyanate, HMDI. No cures were obtained with this curative system and gassing was observed on the surface of the sample.

(U) Additional mixes were made with the cure catalyst chromic 2-ethyl hexoate and H₁₂MDI and DMM as the curatives. In this series, good cures were obtained with the H₁₂MDI-containing mixes. However, the DMM curative failed to give adequately cured propellant. In past mixes with DMM curative, the propellant had cured well using DBTDA and FeAA as the cure catalysts.

b. Propellant Development

(C) A micromixer capable of processing up to 50 g of high energy propellant was designed, fabricated, and placed in operation during this quarter. The micromixer itself is installed in an inert atmosphere box. This box is equipped with two socket-type tongs and has been designed to withstand the detonation of 100 g of composition B. A number of aluminum and HAP propellant formulations have now been made in this equipment. Because this mixer is not of the high-shear type, it is necessary to hold the AlH₃ loadings to a relatively low percentage. At present, an arbitrary limit of 15% AlH₃ was established. Previous studies with AlH₃ established that at this level problems with curative or incompatibility will be evaluated sufficiently to

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TABLE IV
(U) HAND MIX FORMULATIONS

Formulation No.	178-128-1	178-128-2	178-128-3	178-128-4	178-128-5	178-128-6	178-132-1	178-132-2	178-132-3
PREP	29.47	29.47	29.47	29.47	29.47	29.47	30.57	30.57	30.57
TVOPA	29.47	29.47	29.47	29.47	29.47	29.47	30.57	30.57	30.57
Curative	6.08	6.08	6.08	6.08	6.08	6.08	3.86	3.86	3.86
Curative type	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	HMDI	HMDI	HMDI
1,2,6-HT	0.77	0.77	0.77	0.77	0.77	0.77	0.79	0.79	0.79
Catalyst	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32
Catalyst type	VaOAA	TIOAA	DBTDL	VaOAA	TIOAA	DBTDL	VaOAA	TIOAA	DBTDL
Al	10.96	10.96	10.96	---	---	---	10.96	10.96	10.96
LMH-1	---	---	---	10.96	10.96	10.96	---	---	---
HAP	21.93	21.93	21.93	21.93	21.93	21.93	21.93	21.93	21.93
Triol/PREP(OH)	1.47	1.47	1.47	1.47	1.47	1.47	1.49	1.49	1.49
NCO/OH	1.44	1.44	1.44	1.44	1.44	1.44	1.47	1.47	1.47

Formulation No.	178-132-4	178-132-5	178-132-6	178-134-1	178-134-2	178-134-3	178-134-5	178-134-6	178-134-7
PREP	30.57	30.57	30.57	29.38	29.38	29.38	29.45	29.45	29.45
TVOPA	30.57	30.57	30.57	29.38	29.38	29.38	29.45	29.45	29.45
Curative	HMDI	HMDI	HMDI	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI	DMM	DMM	DMM
Curative type	3.86	3.86	3.86	6.19	6.19	6.19	6.14	6.14	6.14
1,2,6-HT	0.79	0.79	0.79	0.84	0.84	0.84	0.75	0.75	0.75
Catalyst	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32	1.32
Catalyst type	VaOAA	TIOAA	DBTDL	Cr ₂ Eth	Cr ₂ Eth	Cr ₂ Eth	Cr ₂ Eth	Cr ₂ Eth	Cr ₂ Eth
Al	---	---	---	10.96	---	10.96	10.96	---	10.96
LMH-1	10.96	10.96	10.96	---	10.96	---	---	10.96	---
AP	---	---	---	21.93	---	---	21.93	---	---
HAP	21.93	21.93	21.93	---	21.93	21.93	---	21.93	21.93
Triol/PREP(OH)	1.49	1.49	1.49	1.60	1.60	1.60	1.44	1.44	1.44
NCO/OH	1.47	1.47	1.47	1.39	1.39	1.39	1.50	1.50	1.50

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allow scaling factors to be made once the system is taken to a high-shear mixer. Table V contains the formulations processed of AlH_3 and HAP propellant

(C) Aluminum hydride formulations UTX 8455 and UTX 8457 with H_{12} MDI both cured firmly at an ambient cure temperature. UTX 8455 had a tensile value of 121 psi and an elongation of 51.8%, and UTX 8457 had values of 45 psi and 93.4%. The latter formulation had 2 days less cure time which could account for the difference in physical properties. These two formulations had impact values of 4.2 kg-cm and had similar sensitivities of friction, both being sensitive on the Esso friction tester with no grit. Autoignition values also were similar with a 30-sec value of approximately 480°F and a 10-sec value of approximately 570°F . These formulations are as stable as those with aluminum as far as autoignition goes, but are much more impact sensitive and friction sensitive.

(C) To determine the extent of cure obtained at ambient temperatures, formulations UTX 8455, 8456, and 8457 were post-cured at 120°F . The further cure was followed by measuring the increase in Shore A hardness values. These data are shown in table VI. The zero Shore A readings were the readings at the conclusion of the ambient cure period. Near maximum values of approximately 70 were obtained after 4 days of additional cure on all specimens. Physical property data have not yet been obtained on this optimally cured propellant but are expected to be near that obtained on conventional aluminized propellant.

(C) Formulation UTX 8459 which contained HAP as an oxidizer yielded a soft cure. The propellant reacted with moisture while being trimmed outside of the dry box and was discarded. It is apparent that stringent handling techniques and moisture disciplines will be required to permit the successful processing and handling of HAP propellant.

(C) Formulations UTX 8460 and UTX 8461 were made to compare the effects of AlH_3 with aluminum in a HAP propellant. Soft cures were obtained in both of these propellants, but no void formation or gassing was observed. Further data are not available at this time on these two propellant systems.

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TABLE V

(U) LMH-1/HAP PROPELLANT FORMULATIONS

Formulation No.	UTX 8455-1	UTX 8456-1	UTX 8457-1	UTX 8458-1	UTX 8459-1
PBEP	19.86	20.56	19.83	19.83	24.30
TVOPA	19.86	20.56	19.83	19.83	24.30
1,2,6-HT	0.49	0.51	0.49	0.49	0.60
Cure catalyst	0.70	0.70	0.70	0.70	0.70
Catalyst type	DBTDA	DBTDA	DBTDA	DBTDL	DBTDA
Curative	4.09	2.67	4.15	4.15	5.10
Curative type	DMM	TDI	H ₁₂ MDI	H ₁₂ MDI	H ₁₂ MDI
LMH-1	15.00	15.00	15.00	15.00	10.00
AP	40.00	40.00	40.00	40.00	---
HAP	---	---	---	---	35.00
Triol/PBEP(OH)	1.4	1.4	1.4	1.4	1.4
NCO/OH	1.5	1.5	1.5	1.5	1.5
Cure time (days) at ambient	7	5	5	5	5
Remarks	Firm cure	Soft cure	Cured, some voids	Soft cure	Soft cure, porous

Formulation No.	UTX 8460	UTX 8461
PBEP	24.35	22.82
TVOPA	24.35	22.82
Curative	5.00	4.69
Curative type	DMM	DMM
1,2,6-HT	0.60	0.57
Catalyst	0.70	0.70
Catalyst type	DBTDA	DBTDA
LMH-1	10.00	---
Al (H-5)	---	9.00
HAP	35.00	39.40
Triol/PBEP(OH)	1.4	1.4
NCO/OH	1.5	1.5
Cure time (days) at ambient	7	7
Remarks	Soft cure	Soft cure

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TABLE VI
(U) PROPELLANT SHORE A DATA

Formulation No.	Days at 120° F after Ambient Cure						
	<u>0</u>	<u>1</u>	<u>3</u>	<u>4</u>	<u>8</u>	<u>9</u>	<u>11</u>
UTX 8455-1	53.5	64	75	75	77	76	76
UTX 8456-1	20	39	70	68.5	70	76	81
UTX 8457-1	36	54.5	67	66	71	75	77

4. PBEP LOT EVALUATION

(C) The series of formulations listed in table VII were cure tests for PBEP lot No. 9557-99A. This is a large lot of PBEP received from Shell Development containing 8 lb of material. This lot has been used extensively in recent studies. The lot cured well in 72 hr at 120° F with triol/PBEP (OH) ratios ranging from 0.85 to 1.05 and NCO(OH) ratios from 0.97 to 1.05. However, it was observed that the cured gumstocks were more opaque than had been noted in cures of previous lots. This phenomenon is discussed in detail in later sections.

TABLE VII
(U) PBEP LOT NO. 9557-99A GUMSTOCK
EVALUATION FORMULATIONS

Formulation No.	215-130-1	215-130-2	215-130-3	215-130-4	215-130-5
PBEP	44.64	44.25	44.05	43.95	44.84
TVOPA	44.64	44.25	44.05	43.95	44.84
TDI	7.86	8.41	8.85	9.03	7.71
1, 2, 6-HT	1.98	2.05	2.05	2.15	1.81
DBTDA	0.89	0.88	0.88	0.88	0.90
Triol/ PBEP(OH)	0.94	1.0	1.00	1.05	0.87
NCO/OH	0.96	1.0	1.05	1.05	0.97
Cure at 120° F, hr	72	72	72	72	72
Remarks	Well cured	Well cured	Well cured	Well cured	Well cured

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5. SCALEUP FORMULATION STUDIES

(U) The last quarterly report discussed in detail the problem of obtaining successful cures when scaling up the PBEP formulation to a 4-lb propellant mix. Recently, the ARC mixes, which at one time cured reproducibly, have failed to yield reproducible cures. The formulations processed during this quarter, listed in table VIII, include mixes made both in the ARC and the 2-quart Bramley-Bekin mixer. Numerous variations such as in the use of cure catalysts, cure level, catalyst level, etc., have been evaluated during this report period. The normal processing studies that were conducted during this report period were implemented with a heavy laboratory effort to try to determine the source of the failure to cure of the PBEP propellant. This work is discussed in section 6.

(U) Formulation UTX 8426-1 was cast as microdogbones for the aging studies. This formulation gave a slow cure with some voids in the propellant. With some change in cure ratios in UTX 8427-1, the propellant cured very well in 2 days. UTX 8427-2 was a further scaleup to the Bramley-Bekin mixer from the ARC. This propellant failed to cure. A fourth mix UTX 8427-3 in the ARC mixer gave a good cure, but with some voids.

(U) It was felt that water was possibly reacting with the diisocyanate and causing poor cures and gassing. The diisocyanate-to-hydroxyl ratio was increased in formulation UTX 8428-1 and -2 with increased mix times after diisocyanate addition. The possibility of a diisocyanate completing any interfering reaction prior to casting with enough TDI left over for cure was considered a procedure that might give good propellant. Both mixes, however, failed to cure and exhibited extreme gassing during casting.

(U) H_{12} MDI, a relatively new diisocyanate with an apparent lower reaction rate than TDI, was used in UTX 8429-1. This propellant cured but gassed severely. UTX 8430-1 utilized DMM which has an even slower reaction rate than H_{12} MDI, gave no gassing during casting, cured well at 120° F, and also appeared to be curing well at ambient temperatures. DMM is well known to have an apparently slow reaction rate with water and was considered an ideal candidate for this propellant system.

(U) To further evaluate DMM a series of mixes UTX 8430 to UTX 8431 were made. UTX 8430-2, -3, and -10 were the only DMM mixes that were made following the initial mix which cured properly. However, no data were obtained from batch 10, as it cured too rapidly to be cast successfully. UTX 8430-2 and -3 did allow the obtaining of a number of microdogbone samples for surveillance studies that will allow comparative data to be obtained between the use of DMM and TDI as the curative. The rest of the mixes in that section either cured very slowly to give soft propellant or failed to cure.

TABLE VIII

(U) PROPELLANT FORMULATIONS*

Formulation No.	UTX									
	8422-11	8422-12	8422-13	8422-14	8422-15	8422-16	8425-1	8423-2	8418-3	
PBEP	18.31	18.31	18.31	18.31	18.31	18.31	18.31	18.31	18.46	
PBEP lot	9557-84	9557-84	9557-84	9557-84	9557-84	9557-84	9557-84	9557-84	9546-16	
Plasticizer	18.31	18.31	18.31	18.31	18.31	18.31	18.31	18.31	18.46	
Type of plasticizer	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	DBP	TVOPA	TVOPA	
Diisocyanate	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.18	2.21	
Type of diisocyanate	TDI	TDI	TDI	TDI	TDI	TDI	TDI	TDI	TDI	
1,2,6-HT	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	
Catalyst	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.46	
Catalyst type	FeAA	FeAA	FeAA	FeAA	FeAA	FeAA	FeAA	DBTDA	FeAA	
Al	13.01	13.01	13.01	13.01	13.01	13.01	13.01	13.01	13.05	
AP	47.05	47.05	47.05	47.05	47.05	47.05	47.05	47.05	46.86	
Triol/PBEP (OH)	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	1.55	
NCO/OH	0.98	0.98	0.98	0.96	0.96	0.98	0.98	0.98	1.30	
Cure at 120° F, hr	72	72	72	72	72	72	72	72	72	
Remarks	Soft cure, voids	Well cured	Soft cure, voids	Soft cure, voids	Soft cure, voids	Soft cure, voids	Soft cure, voids	Cured, no voids	Soft cure, voids	

Formulation No.	UTX							
	8426-1	8427-1	8427-2	8427-3	8428-1	8428-2	8429-1	8430-1
PBEP	17.98	17.97	17.97	17.97	17.86	17.86	17.69	17.68
TVOPA	17.98	17.97	17.97	17.97	17.86	17.86	17.69	17.68
Diisocyanate	3.17	3.25	3.25	3.25	3.86	3.86	4.76	4.81
Type of diisocyanate	TDI	TDI	TDI	TDI	TDI	TDI	H ₁₂ MDI	DMM
1, 2, 6-HT	0.80	0.75	0.75	0.75	0.74	0.74	0.74	0.74
Catalyst	0.64	0.64	0.64	0.64	0.63	0.63	0.64	0.63
Catalyst type	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
Al	12.99	12.98	12.98	12.98	12.90	12.90	12.78	12.77
AP	46.46	46.43	46.43	46.43	46.14	46.14	45.71	45.63
Triol/PBEP (OH)	0.96	0.90	0.90	0.90	0.89	0.89	0.90	0.90
NCO/OH	0.95	1.00	1.00	1.00	1.20	1.20	1.00	1.00
Cure at 120° F, hr	120	48	120	120	120	120	120	120
Remarks	Cured, some voids	Well cured	Uncured	Cured, some voids	Uncured	Uncured	Cured, gassing	Well cured

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(OH)
NCO/OH 0.95 1.00 1.00 1.00 1.20 1.20 0.89 0.89 0.90 0.90 0.90
Cure at 120 48 120 120 120 120 120 120 120 120 120
120° F, hr
Remarks Cured, some voids Well cured some voids Cured, gassing Well cured
Mixer ARC ARC BB ARC BB ARC ARC

Formulation No.	UTX									
	8427-4	8427-5	8430-2	8430-3	8430-4	8430-5	8430-6	8430-7	8430-8	8430-9
PBEP	17.97	17.97	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68
TVOPA	17.97	17.97	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68
Diisocyanate	3.25	3.25	4.81	4.81	4.81	4.81	4.81	4.81	4.81	4.81
Type of diisocyanate	TDI	TDI	DMM	DMM	DMM	DMM	DMM	DMM	DMM	DMM
1,2,6-HT	0.75	0.75	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Catalyst	0.64	0.64	0.63	0.63	0.63	0.63	0.63	0.63	0.63	0.63
Catalyst type	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
Al	12.98	12.98	12.77	12.77	12.77	12.77	12.77	12.77	12.77	12.77
AP	46.43	46.43	45.68	45.68	45.68	45.68	45.68	45.68	45.68	45.68
Triol/PBEP (OH)	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
NCO/OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cure at 120° F, hr	120	96	168	120	96	120	96	120	96	120
Remarks	No cure, voids	Soft cure	Well cured	Cured	Soft cure, voids	No cure, voids	Soft cure, voids	Cured	Soft cure, voids	No cure, voids

Formulation No.	UTX									
	8430-6	8430-7	8430-8	8430-9	8430-10	8431-1	8431-2	8431-3	8431-4	8431-5
PBEP	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68
TVOPA	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68	17.68
Diisocyanate	4.81	4.81	4.81	4.81	4.81	4.81	4.81	4.81	4.81	4.81
Type of diisocyanate	DMM	DMM	DMM	DMM	DMM	DMM	DMM	DMM	DMM	DMM
1,2,6-HT	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Catalyst	0.63	0.63	0.63	0.63	0.63	0.63	0.63	0.63	0.63	0.63
Catalyst type	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
Al	12.77	12.77	12.77	12.77	12.77	12.77	12.77	12.77	12.77	12.77
AP	45.68	45.68	45.68	45.68	45.68	45.68	45.68	45.68	45.68	45.68
Triol/PBEP (OH)	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
NCO/OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cure at 120° F, hr	120	330	330	120	---	330	---	330	---	330
Remarks	No cure, voids	Soft cure	Soft cure	No cure, voids	Cured	Soft cure	No cure, voids	Cured	Soft cure	Soft cure

* All the mixes listed as giving soft cures after 72 hr at 120° F postcured in an additional 7 to 10 days at ambient to give very tough, flexible propellant.

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(U) In UTX 8423-2, which was processed in the 2-quart Bramley-Bekin mixer, FeAA was replaced by DBTDA to evaluate the effect of cure catalyst upon the cure. This propellant gave a somewhat slow cure but was void free. Four 1-lb motors were obtained in this formulation and have subsequently been incorporated into the surveillance study. Repeating this mix in subsequent scaled up formulations failed to reproduce the cure obtained on the original mix.

(C) The tensile properties listed in tables IX and X indicate a high degree of crosslinking for all systems except UTX 8422-10, in table IX, which had no postcure. This formulation with postcure gave a tensile value increasing from 45.9 psi to 118 psi and elongation decreasing from 16.5% to 12.6%. Because a rapid reaction of diisocyanate and triol has been noticed, it would be expected that crosslinking would predominate over chain extension resulting in high tensile and low elongation values after complete cure.

TABLE IX

(U) TENSILE PROPERTIES

Formulation No.	Measured Data		
	Tensile psi	Elongation %	Temperature ° F
UTX 8422-2	200	14.6	76
UTX 8422-10	45.9	16.5	76
UTX 8430-1	139	11.9	76

TABLE X

(U) TENSILE PROPERTIES AT VARIOUS TEMPERATURES

Formulation No.	Measured Data		
	Tensile psi	Elongation %	Temperature ° F
UTX 8422-10	60.6	14.3	+140
	70.5	11.0	+120
	118	12.6	+76
	435	18.0	+10
	478	10.6	0
	614	9.3	-10
	654	11.3	-20

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(C) The values at various temperatures listed in table X show the expected trend of 60.6 psi at +140° F to 654 psi at -20° F. The elongation values are irregular, possibly caused by the testing of only one sample at each temperature. However, no great drop in elongation was noted at least to -20° F. The elongation value at -20° F was 11.3% compared to an average value over the complete range of 12.4%.

6. BINDER CONTAMINATION STUDIES

(C) Because most scaleup mixes failed to cure properly, samples of binder containing equal amounts of PBEP and TVOPA were taken from the Bramley-Bekin mixer at various times for water and solvent analysis by GLC at Shell Development. After evaporation of methylene chloride solvent overnight at 110° F, the system was evacuated for 5 hr. Samples of the binder were taken at 2.5, 3.5, and 5 hr after vacuum was initiated. As shown in table XI, the water content dropped to 0.066% after 5 hr from the previous high of 0.087% at 2.5 hr. The methylene chloride solvent dropped from 0.25% to 0.083% during the same period. Neither the solvent nor water content appeared to be large enough to completely retard propellant cure. However, if even small amounts of moisture are introduced with other ingredients such as AP (ammonium perchlorate) and aluminum, this value may have more significance in retarding cure and causing gassing. A small percentage of residual acetone probably remains in the PBEP from the preparation.

TABLE XI
(U) ANALYSIS* OF A PBEP-TVOPA† MIXTURE

<u>Evacuation Time, hr</u>	<u>Contamination (wt-%)</u>		
	<u>Water</u>	<u>Methylene Chloride</u>	<u>Acetone</u>
2.5	0.087	0.259	0.018
3.5	0.083	0.156	0.015
5.0	0.066	0.083	0.012

* These analyses were run on a GLC by Shell Development Corporation.

† PBEP lot number was 9557-99A. GLC of Shell's retainer sample of this lot gave a value of 0.013% water in the solution or 0.04% based on PBEP.

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7. PBEP/TVOPA MISCIBILITY STUDY

(U) Aerojet-General has reported that TVOPA is not completely miscible with PBEP at equal levels. Because some opacity was noted in the lot evaluation of 9557-99A, and because poor cures have been obtained with later lots of PBEP, a study was initiated in the laboratory to determine the cause of this apparent binder separation. Numerous gumstock samples shown in table XII were prepared for this study.

(C) Formulation 215-138 was a 200-g gumstock mix. This material was milky when cast from the mixer and failed to cure in several days. Microscopic examination of the uncured binder was inconclusive. The uncured binder was extracted with acetone, and an insoluble white residue remained. This residue was insoluble in the several common organic solvents tried, did not react with sodium hydroxide, but did react with sulfuric acid. Infra-red analysis indicated that it was not PBEP, contained some NCO, had aliphatic C-H and carbonyl groups. Partial reaction of the TDI would cause cure problems and perhaps could be the reason for the slow cures obtained in the scaleup mixes. The formation of this precipitate also explained the reported opacity of the PBEP/TVOPA gumstock during the initial cure time.

(U) Several hand mixes were prepared from three lots of PBEP to check if this opacity was unique in one lot or a group of lots. All hand mixes were milky after a few minutes of heating. Formulation 215-14-2 using FeAA instead of DBTDA as in 215-14-1 had the same opaqueness. Mixes 215-146 and 215-150 using DMM instead of TDI appeared the same except that 215-146 cured in 3 hr instead of 24 hr. Reducing the percent of TVOPA to only 60% of the normal amount gave the same type of opaqueness as the higher plasticized gumstock.

(U) Formulations 215-164-1 and -2 were prepared to test the effect of 1, 2, 6-HT versus glycerol in the same formulations. The white precipitate appeared about 10 min after addition of all ingredients in each case. Even with heating after stepwise addition of each component, no cloudiness was observed until the binder system was complete.

(U) Mix number 215-167 was prepared with dibutyl phthalate in place of TVOPA. Again the turbidity occurred although not as great as with TVOPA.

(U) Series 215-168-1, -2, -3, and -4 was a test of various ingredients other than PBEP and TVOPA obtained from Shell Development Co. and compared to the ingredients used at UTC. By systematically replacing UTC ingredients of triol, TDI, and DBTDA with one from Shell, it was hoped to establish if the precipitate was caused by an impurity in one of the ingredients. All samples cured well but with the same opaqueness.

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(C) Because solvent and/or water retention might be part of the problem, a PBEP/TVOPA mixture was stripped at 80° C instead of the usual 50° C for several hr. A sample was sent to Shell Development for analysis by GLC. The water percentage was 0.069% which was similar to the percentage found in a sample stripped in a mixer at 50° C. However, no acetone was found, and the methylene chloride level dropped from 0.083% in the 50° C sample to 0.005% in the 80° C stripped material. Because it may be difficult to remove moisture below this level (at a reasonable temperature) by vacuum stripping, the binder materials are now being dried over molecular sieves while in solvent.

(C) During some joint laboratory work at Shell, a formulation was prepared where only 10% of the normal triol level was inadvertently added. It was noticed that no precipitate occurred in this sample. Therefore, series 215-170-1, -2, -3, and -4 was prepared to test the effect of various triol levels on precipitate formation. This extreme cloudiness dropped significantly below a triol/PBEP(OH) ratio of 0.7. The cloudiness is not caused by an impurity, but merely by a rapid reaction of the triol and diisocyanate as compared to the reaction of PBEP and diisocyanate. This separation could be part of the scaleup problem. The effect would not be as noticeable in propellant from the ARC mixer as in the Bramley-Bekin because of the smaller sample size and much more efficient mixing in the ARC.

(C) To evaluate the effect of the triol on propellant cure, several mixes were made where the triol content was reduced. These mixes failed to cure properly but were considered marginally improved over the standard compositions. In another mix the effect of adding triol after the curative was evaluated. Approximately one third of the triol was added normally, and the remainder was added after the curative. The mix time between addition of curative and final triol was also increased. However, the results of this mix were questionable as part of the samples were well cured and part were not.

(C) In another mix a prepolymer of the PBEP and TDI was made by reacting the PBEP and TDI for 50 min prior to adding the triol. To get the PBEP-NCO reaction to proceed the DBTDA catalyst level was raised to approximately 1.4%. Upon addition of triol the crosslinking reaction proceeded too rapidly to permit the propellant to be cast.

(C) Therefore, it appears that it will be necessary to control catalyst level, mix time, and temperature in a way that the PBEP-NCO reaction will occur properly. Yet, when the triol is added a runaway crosslinking reaction does not occur. This possibly can be achieved by mixing hot prior to triol addition and then cooling the mix to slow down the triol-NCO reaction. Another approach being examined is the use of the triols with lower reaction rates with NCO groups than the currently used 1, 2, 6-HT.

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(U) HAND MI

<u>Formulation No.</u>	<u>215-164-1†</u>	<u>215-164-2†</u>	<u>215-167†</u>	<u>215-168-</u>
PBEP	44.29	44.53	44.29	44.48
PBEP lot	9557-99A	9557-99A	9557-99A	9557-99
Plasticizer	44.29	44.53	44.29‡	44.48
Type of plasticizer	TVOPA	TVOPA	DBP	TVOPA
Diisocyanate	7.99	8.04	7.99	8.01
Type of diisocyanate	TDI	TDI	TDI	TDI
Triol	1.84	1.29	1.84	1.26
Type of triol	1, 2, 6-HT	Glycerol	1, 2, 6-HT	Glycerol
Catalyst	1.56	1.60	1.56	1.78
Type of catalyst	DBTDA	DBTDA	DBTDA	DBTDA
Triol/PBEP(OH)†	0.87	0.87	0.87	0.87
NCO/OH‡	1.02	1.02	1.02	1.02
Cure at 120° F, hr	24	24	24	48
Remarks	Cured	Cured	Cured	Cured

<u>Formulation No.</u>	<u>215-138†</u>	<u>215-139†</u>	<u>215-140-1§</u>	<u>215-140-</u>
PBEP	44.29	44.25	45.77	45.77
PBEP lot	9557-99A	9557-99A	9557-84	9557-84
TVOPA	44.29	44.25	45.77	45.77
Diisocyanate	8.00	7.99	5.49	5.49
Type of diisocyanate	TDI	TDI	TDI	TDI
Triol	1.85	1.84	1.25	1.25
Type of triol	1, 2, 6-HT	1, 2, 6-HT	1, 2, 6-HT	1, 2, 6-HT
Catalyst	1.57	1.59	1.65	1.65†
Type of catalyst	DBTDA	DBTDA	DBTDA	FeAA
Triol/PBEP(OH)	0.90	0.90	1.58	1.58
NCO/OH	1.00	1.00	1.32	1.32
Cure at 120° F, hr	72	24	24	24
Remarks	Uncured	Cured	Cured	Cured

* All values for ingredients are in weight percent.

† The triol/PBEP(OH) and NCO/OH ratios are based on 0.108 hydroxyl equivalent.

‡ DBP substituted for TVOPA in this mix.

§ The triol/PBEP(OH) and NCO/OH ratios are based on 0.041 hydroxyl equivalent.

** DMM substituted for TDI in these mixes.

†† FeAA substituted for DBTDA in this mix.

TABLE XII

D MIXES FOR LABORATORY STUDIES

<u>168-1†</u>	<u>216-168-2†</u>	<u>215-168-3†</u>	<u>215-168-4†</u>	<u>215-170-1†</u>	<u>215-170-2†</u>	<u>215-170-3†</u>	<u>215-170-4†</u>
4.48	44.25	44.25	44.98	45.62	45.33	45.03	44.74
97-99A	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A	9557-99A
4.48	44.25	44.25	44.98	45.62	45.33	45.03	44.74
TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA	TVOPA
8.01	7.96	7.96	8.10	6.07	6.46	6.85	7.25
TDI	TDI	TDI	TDI	TDI	TDI	TDI	TDI
1.26	1.78	1.78	0.13	0.87	1.07	1.28	1.49
Glycerol	1,2,6-HT	1,2,6-HT	Glycerol	1,2,6-HT	1,2,6-HT	1,2,6-HT	1,2,6-HT
1.78	1.77	1.77	1.80	1.82	1.81	1.80	1.79
DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
0.87	0.87	0.87	0.87	0.40	0.50	0.60	0.70
1.02	1.02	1.02	1.74	1.00	1.00	1.00	1.00
8	48	48	48	48	48	48	48
Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured

<u>140-2§</u>	<u>215-141§</u>	<u>215-142†</u>	<u>215-143§</u>	<u>215-144§</u>	<u>215-145§</u>	<u>215-146§</u>	<u>215-150†</u>
5.77	45.77	57.61	60.74	60.74	45.77	44.35	53.76
7-84	9546-16	9557-99A	9546-16	9557-84	9557-84	9557-84	9557-99A
5.77	45.77	24.69	26.03	26.03	45.77	44.35	23.03
5.49	5.49	12.41	8.70	8.70	5.49	8.42**	18.23*
TDI	TDI	TDI	TDI	TDI	TDI	DMM	DMM
1.25	1.25	2.86	1.98	1.90	1.25	1.20	2.68
1,6-HT	1,2,6-HT	1,2,6-HT	1,2,6-HT	1,2,6-HT	1,2,6-HT	1,2,6-HT	1,2,6-HT
1.65††	1.65	2.47	2.60	2.60	1.65	1.60	2.30
neAA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA	DBTDA
1.58	1.58	0.70	1.58	1.58	1.58	1.58	0.90
1.32	1.32	1.00	1.32	1.32	1.32	1.32	1.00
24	24	24	24	24	24	3	24
Cured	Cured	Cured	Cured	Cured	Cured	Cured	Cured

† equivalents per 100 grams of polymer as determined by gel time studies by Shell Development.

§ equivalents per 100 grams of polymer as determined by infrared by Shell Development.

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(U) Cyclohexyl triisocyanate (CTI), a trifunctional isocyanate made by Aerojet-General Corporation, is also being evaluated. Initial gumstock evaluation gave good cures. Because this eliminates the need for a triol in the system, further cure studies with CTI and mixtures of CTI and difunctional isocyanates are being carried out.

8. NFPA BINDER EVALUATION

(C) Currently, there are only limited data available comparing PBEP with the Rohm and Haas NFPA binder. The Rohm and Haas binder is based upon 2,3-bis(difluoramino) propyl acrylate monomer. The NFPA is polymerized with approximately 5% acrylic acid copolymer to form a prepolymer with carboxy functional groups. This prepolymer is cured by crosslinking with UNOX 221, a diepoxide manufactured by Union Carbide Company.

(U) Samples of Rohm and Haas formulation SE-103A were prepared for both physical property, hazard, and thermal stability evaluation. These results will be directly comparable with PBEP samples under identical test conditions.

(C) Impact sensitivity of the prepolymer (PPAA-3-1011) was 8.0 kg-cm (E₅₀ in OM open cup tester) and 11.0 kg-cm for the cured propellant. Friction sensitivity (Esso tester) for the prepolymer and propellant was (+) Pyrex glass grit at 100 ft/lb and 38 ft/lb, respectively.

(C) The Rohm and Haas formulation SE-103A was scaled up to the ARC mixer, and physical property data were obtained on the propellant. Crosshead values of tensile and elongation were 44.2 psi and 21.9%, respectively. Measured values were 50.4 psi tensile and 15.6% elongation. The tensile values were comparable to those reported by Rohm and Haas, however, elongation was lower than reported. Rohm and Haas, however, did not state whether they were reporting crosshead or measured physical properties. Further samples will be prepared for aging studies and high temperature surveillance studies following scaleup to the 250-g batch size.

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SECTION III

CONCLUSIONS AND FUTURE WORK

(C) It now appears that the cause of the PBEP cure problem has been found. Reduction of triol content, use of less reactive triols and elimination of triols by use of tri- and polyfunctional isocyanates are being pursued. The addition of triol last, after the curative and PBEP has been permitted to prereact, is also being investigated. Studies on why this problem has occurred only in large batches of PBEP are also continuing. This cure problem has also caused some delay in work on the HAP/ AlH_3 system. However, these systems should be scaled up in the coming quarter, assuming a successful answer to the cure problem is reached.

(U) Further specimens for the surveillance work will be prepared and laboratory studies on thermal stability will be continued.

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13. ABSTRACT (U) Work was continued on studying the cure problem of PBEP propellants. It now appears that a rapid reaction between the isocyanate curative and triol cross-linkers is the source of difficulty. It appears possible that this problem became enhanced by a change in PBEP during synthesis scaleup that resulted in a lower reactivity of the hydroxyl groups. Further investigations of the impact sensitivity of PBEP and PBEP propellants were made. No change in previously reported data was found, and it was concluded that neither PBEP nor propellant was unduly impact sensitive. Good cures were obtained on LMH-1/PBEP propellant. Stress of 121 psi and strain of 52% were obtained on an ambient cured system. Preparation of HAP-containing propellant requires a dry atmosphere throughout the complete operation. The cured propellant also must be protected from moisture. Surveillance studies of 2-in. cubes have indicated that DBTDA cure catalyst has better aging characteristics.			

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